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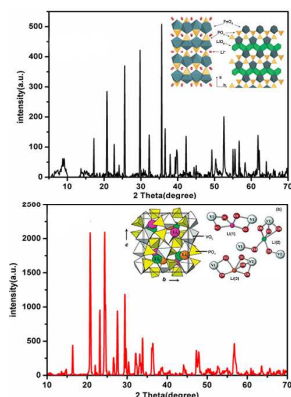
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TOC Keyword: $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite materials, modification, electrochemical performances

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Effect of ion doping on electrochemical performances of $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite cathode materials

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REVIEWS

Effect of ion doping on electrochemical performances of LiFePO_4 /

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite cathode materials

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Due to the low intrinsic electronic and ionic conductivities, olivine-structured LiFePO_4 has been the focus of research in ionic modifications of LiFePO_4/C cathode materials. Various ionic doping processes have been developed for enhanced electrochemical performances of lithium ion batteries, including cation and anion doped modifications of LiFePO_4 . In particular, recently significant progress has been made in understanding and controlling synthesis, nanostructure and electrochemical performances of the $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite materials. However, there are still many challenges in achieving greatly the charge transfer kinetics and the charge/discharge performance of a $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite cathode. In this review, we summarize some of the recent progress of several typical cation modification methods.

Introduction

Due to the rapid depletion of non-renewable resources and the effects of global warming, people's attention has been attracted on electric vehicles (EVs) or hybrid electric vehicles (HEVs) and energy storage devices. The cathode material is the most important component for lithium-ion battery with high-energy density, high-rate capability and long cycle life. It should be one of the main issues to choose cathode materials for the large-scale lithium-ion batteries. Among those cathode materials, olivine structured LiFePO_4 (LFP) and monoclinic structured $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) attract the most attention, due to its intrinsic structural and chemical stability that leads to safe and long cycle life batteries, as well as low cost. LFP and LVP have been

considered as the most competitive cathode candidates for the next-generation large-scale lithium-ion battery used for HEVs or EVs. However, one of the main obstacles for practical applications of LFP and LVP is its poor rate capability, which can be attributed to slow kinetics of lithium-ion diffusion coefficient and the poor electronic conductivity.¹⁻³

Pure LFP is an electronically conductive material consisting mainly of N-type semiconductor. It has a theoretical capacity of 170 mAh g^{-1} at a voltage of 3.45 Volt versus lithium, lithium-ion diffusion coefficient of 10^{-14} to 10^{-16} $\text{cm}^2 \text{ s}^{-1}$ and electron conductivity of 10^{-9} to 10^{-10} S cm^{-1} .^{4,5} Prosini et al measured the lithium ion migration parameter value of approximately -3.8 (when the lithium ion migration is 0, g is -4).⁶ Pure LVP has a low electronic conductivity of about 2.3×10^{-8} S cm^{-1} at 27°C,⁷ which presents a major drawback for the practical implementation of materials.

In order to improve the properties of existing LiFePO_4 -based electrode materials, extensive efforts have been made by electrochemical researchers, which include particle size control

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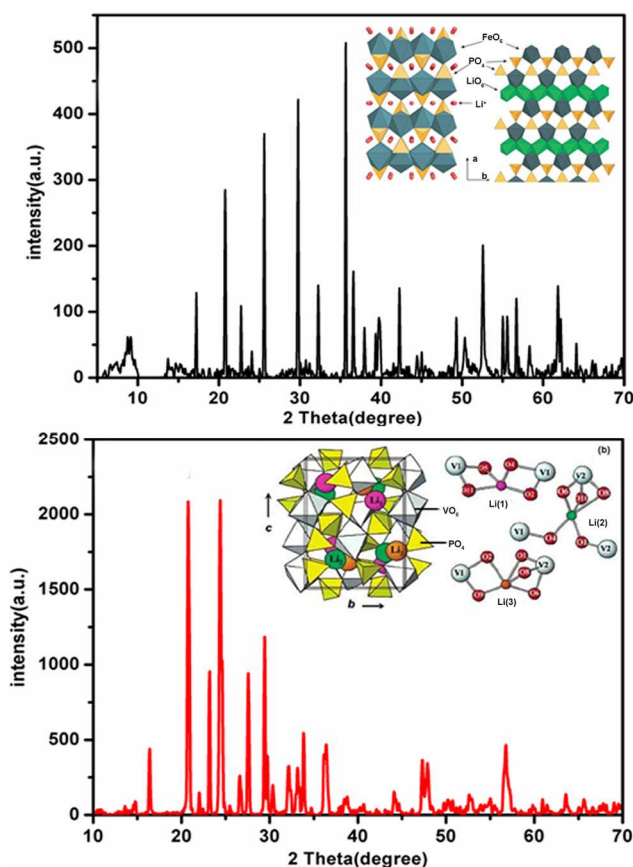


Fig. 1 The crystal structure of olivine LiFePO_4 in projection along $[001]$ ²⁷ and its XRD profiles (a); the crystal structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ¹⁸ and its XRD profiles (b).

and manipulation, surface modification of particles by coating with electronically conductive agents, and atomic-level doping with supervalent ions.⁸⁻¹⁰ One early report that spanned much activity suggested that the poor electronic conductivity could be raised by 8 orders of magnitude by supervalent-cation doping, which was proposed to stabilize minority Fe^{3+} hole carriers in the lattice.¹¹ The dramatic increase in conductivity was later implicated to be instead partly the result of carbon, and also metallic iron phosphides/carbophosphides on the LiFePO_4 surface arising from solid-state reactivity at the elevated temperatures used in processing.¹² In 2002, Chung et al.¹¹ investigated different cation dopants to determine the effects of aliovalent doping on the electronic conductivity of LiFePO_4 . In 2012, Park et al.¹³ demonstrated that the undercoordinated $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple at the surface gives a high barrier for charge transfer, but it can be stabilized by nitrogen or sulfur anion surface modification. The surface modification improves greatly the charge transfer kinetics and the charge/discharge performance of a LiFePO_4 cathode. Reports indicated, via structural and electrochemical analyses, that ion doping could decrease the lithium miscibility gap, favor phase transformation kinetics in cycling, expand diffusion channels, and introduce controlled atomic disorder into the ordered olivine structure.¹⁴

Since the pioneering work of Jiajun Wang and coworkers,²

Table 1 Basic properties of olivine LiFePO_4 and monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ²⁸

	Olivine LiFePO_4 (LFP)	Monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP)
WP(V vs. Li/Li^+)	3.45	3.62, 3.68, 4.08 and 4.55
C (mA h g^{-1})	170 (Theoretical) 150 (Practical)	197 (Theoretical) 160-170 (Practical)
Ed	590 (Whk g^{-1}) (Theoretical) 520 (Whk g^{-1}) (Practical)	2 330 mWh cm^{-3} after carbon coating
Ec (S cm^{-1})	10^{-9} to 10^{-8}	2.3×10^{-8}
Cost ($\text{\$ kg}^{-1}$)	20–25 Possibly low, but limited by patent issues and process cost	Higher than LFP

Note: (a) WP: Working potential; (b) C: Capacity at low C rates (<0.1 C); (c) Ed: Energy density; (d) Ec: Electrical conductivity.

numerous works have been done to investigate the synthesis, structure and electrochemical properties of LiFePO_4 . In the present work, focus is given to the impact of cation modification on the electrochemical performance of $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite cathode. The effective of single and dual dopants for the cathode materials are compared. An insight into the future research and development of $\text{LiFePO}_4/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites is also discussed.

Structure and properties

The structure framework for Olivine-type LiFePO_4 consists of FeO_6 octahedra and PO_4 tetrahedra, space group Pnma, and Li ion locating at the 1D channel along $[010]$ direction with relatively low migration energies.¹⁵⁻¹⁷ One FeO_6 octahedron has common edges with two LiO_6 octahedra. PO_4 groups share one edge with an FeO_6 octahedron and two edges with LiO_6 octahedra. This will greatly limit the transmission speed of the lithium-ion. The monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ possesses a NASICON-type structure consisting of slightly distorted VO_6 octahedra and PO_4 tetrahedra.¹⁸⁻²⁰ $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ contains three independent lithium sites. And the large poly-anions replace the smaller O^{2-} ions in this open framework so as to stabilize the structure and allows fast ion migration. As VO_6 octahedral separated by PO_4 tetrahedra, VO_6 octahedral cannot directly connected with each other, which limits the electron conductivity.²¹⁻²⁶ XRD profiles with the structure of Olivine-type LiFePO_4 and monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as shown in Fig. 1. The other basic properties are shown in Table 1.²⁸

Enhancing the electrochemical performance of $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$

LFP shows low-cost, environmentally friendly and can be cycled thousands of times over years without decay and monoclinic LVP offers the optimal combination of high operating voltage, high lithium capacity, good ion mobility, excellent thermal stability and the highest theoretical capacity of all the phosphates. They are act as potential cathode materials. However, both LFP and LVP have a low electronic conductivity, which presents a major drawback for the practical implementation of EVs or HEVs.

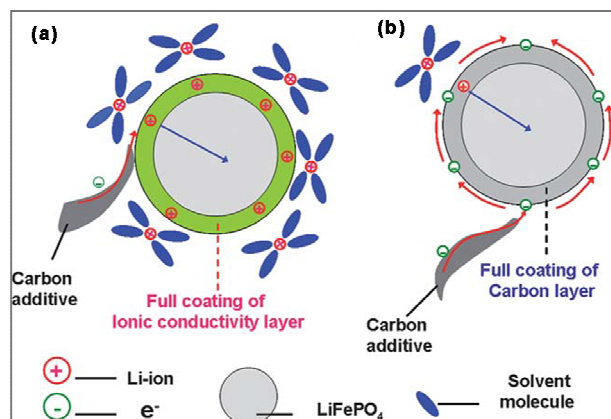


Fig. 2 Schematic representation of LiFePO₄ nano-particles fully coated using (a) an ionic conductivity layer and (b) a carbon layer.⁴⁸

Many efforts have been made to improve the electrochemical performance of LFP and LVP, including nanosizing (so as to shorten the Li ion diffusion length in the solid state as well as decrease the anti-site defect to increase the Li ion conductivity^{29, 30–36} conductive coating,^{37,38} and doping modification.^{9,11,39–42} Except that is preparing LiFePO₄-based compounds with the fast ion conductor additive Li₃V₂(PO₄)₃.^{43–47}

Conductive coating

It is common to use electron and Li⁺ ion conductive coating of LiFePO₄ and Li₃V₂(PO₄)₃ particles, and carbon coating is an effective way to improve the electronic conductivity. Fig. 2 shows schematic representation of LiFePO₄ conductive coating. Organic matter pyrolysis into carbon at high temperature, and the carbon will increase the surface conductivity. Nanometer size particles can be refined grain products, expanding the conductive area which is contribute to diffusion of lithium ions. The introduction of carbon can avoid the formation of Fe³⁺, and provides electron tunneling for phosphate material, to prevent the grain growth, increasing its surface area, and to improve the electrochemical performance of the product. Barker et al.⁴⁹ first introduced a carbothermal reduction method to synthesize Li₃V₂(PO₄)₃/C using carbon black as the carbon source, and the electronic conductivity of the materials was greatly improved by the residual carbon. The pioneering work was carried out by Ravet et al.^{50,51} who showed that LiFePO₄ with a carbon coating can achieve almost the theoretical capacity.

Single doping

When it comes to lithium iron phosphate and lithium vanadium phosphate modification, doping is necessary to enhance their electrochemical properties, and more work has been demonstrated to improve the electrochemical performance. It is necessary to take into account the structure of the materials before doping. Experiments have shown that conductivity of Li_{1-x}M_{2+x}FePO₄ is as 10⁸ times as undoped sample. The XRD results show that the charge compensation by means of point defects, doping in the structure is allowed.^{14,52} LiFePO₄ defect chemistry research provide some acceptable doped of defect compensation mechanism in Table 2.⁵³ Ions tend to be substituted by isovalent ions. A variety of dopants with charges of +1 to +6, including V⁵⁺,^{54,55} Ti⁴⁺,^{56–58} Cr³⁺,⁵⁹ Al³⁺,^{60–62} Nb⁵⁺,^{63,64} Zn²⁺,⁹ Mg²⁺,^{65–67} Mo⁶⁺,⁶⁸ La³⁺,⁶⁹ have been employed for both Li⁺ and M²⁺ substitution in the nano-sized LiFePO₄ or Li₃V₂(PO₄)₃ system. Low favorable energies were found only for Na⁺ substitution on the Li⁺ site and isovalent dopants (e.g., Mg²⁺) on the M²⁺ site. In contrast, aliovalent doping appears unfavorable

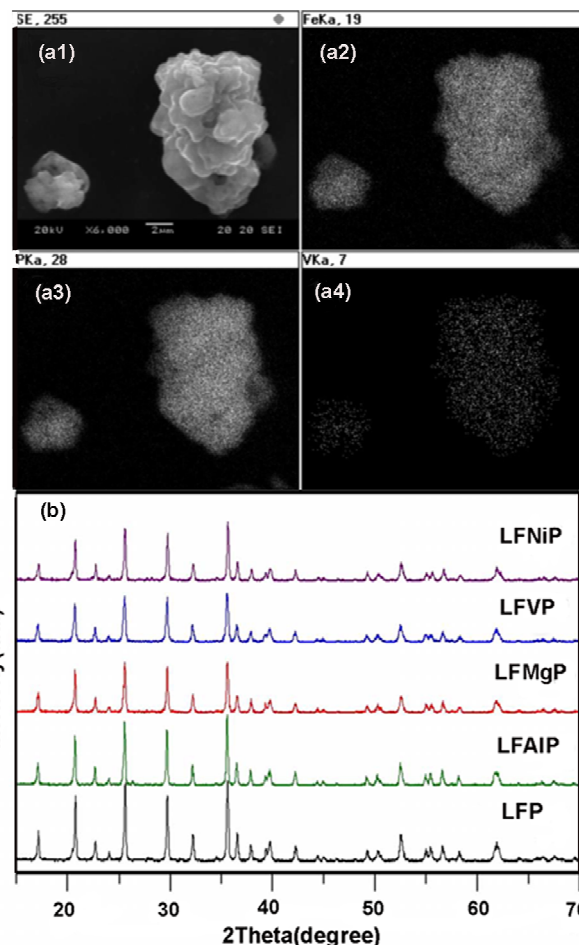


Fig. 3 Elemental mapping and SEM image for LiFe_{0.95}V_{0.05}PO₄ sample. (a1) SEM image of LiFe_{0.95}V_{0.05}PO₄ sample, (a2) elemental mapping for Fe, (a3) elemental mapping for P, (a4) elemental mapping for V; (b) XRD patterns of M-doped LiFePO₄ samples (M=Ni, V, Mg, Al).⁷¹

on both Li⁺ and M²⁺ sites in all four phases.⁷⁰ The SEM images of LiFe_{0.95}V_{0.05}PO₄ with their elemental mappings (Fig. 3a1-a4) and XRD patterns of M-doped LiFePO₄ samples (M=Ni, V, Mg, Al) (Fig. 3b) are verify that the doping element is incorporated in the lithium iron phosphate crystal.⁷¹

After modification, the original performance and high rate performance or cycling performance of two materials have been improved. Na-doped Li_{3-x}Na_xV₂(PO₄)₃/C (x = 0.00, 0.01, 0.03, and 0.05) compounds have been synthesized by using sol-gel method. Li_{2.97}Na_{0.03}V₂(PO₄)₃/C presents the highest initial capacity of 118.9 mAh g⁻¹ and the capacity retention rate was 88% after 80 cycles at 2.0C (Fig. 4a1,a2).⁷² Li₃V_{2-x}Sn_x(PO₄)₃/C cathode materials fast synthesized by a microwave solid-state synthesis method. At a discharge rate of 0.5 C in the potential range of 2.5–4.5 V at room temperature, the initial discharge

Table 2 Defect compensation mechanism for LiFePO₄.⁵³

Ideal crystal composition	Defect compensation mechanism	Defect compensation krogger-vink notation
Li _{1-n} M _y ⁿ⁺ FePO ₄	Li-substitution& Li-vacancy compensation	[V _{Li} [•]] _n =[M _{Li} ⁽ⁿ⁻¹⁾]
Li _{1-(n-2)y} M _y ⁿ⁺ Fe _{1-y} PO ₄	Fe-substitution& Li-vacancy compensation	[V _{Li} [•]] _n =[M _{Fe} ⁽ⁿ⁻²⁾] [V _{Li} [•]] ₂ =[Zr _{Fe} [•]]
Li _{1-y} M _y ⁿ⁺ Fe _{1-(n-1)y/2} PO ₄	Li-substitution& Fe-vacancy compensation	2[V _{Fe} [•]] _n =[(n-1)[M _{Li} ⁽ⁿ⁻¹⁾] 2[V _{Fe} [•]] ₃ =[3Zr _{Fe} [•]]
LiM _y ⁿ⁺ Fe _{1-n/2} PO ₄	Fe-substitution& Fe-vacancy compensation	2[V _{Fe} [•]] _n =[(n-2)[M _{Fe} ⁽ⁿ⁻²⁾] [V _{Fe} [•]] ₁ =[Zr _{Fe} [•]]
LiFePO ₄ +M _x O _y	Stoichiometric&impurity	undetermined

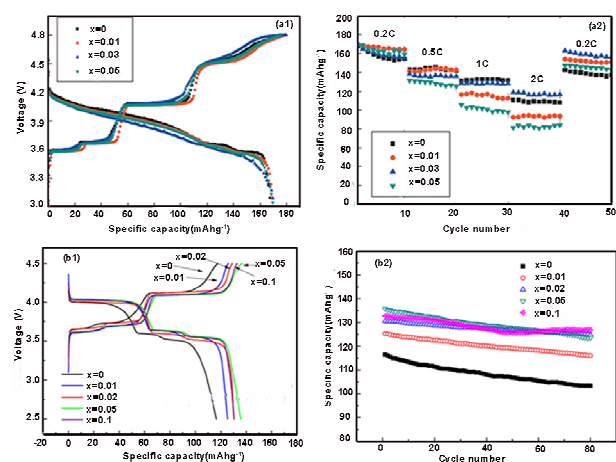


Fig. 4 Charge/discharge and cyclic performances of samples for doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ compounds (Initial charge/discharge curves of $\text{Li}_{3-x}\text{Na}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ ($x = 0.00, 0.01, 0.03, \text{ and } 0.05$) (a1) and rate abilities of 0.2C, 0.5C, 1.0C, 2.0C (a2); initial charge/discharge curves of $\text{Li}_3\text{V}_{2-x}\text{Sn}_x(\text{PO}_4)_3/\text{C}$ ($x = 0, 0.01, 0.02, 0.05, 0.10$) at 0.5 C rate in the voltage range between 2.5 and 4.5 V (b1), and cycle performance comparisons (b2)).^{72, 73}

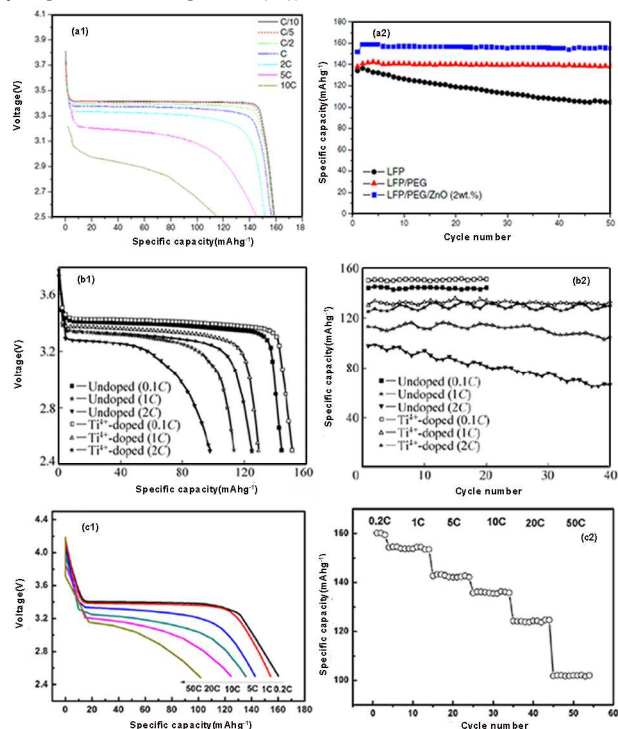


Fig. 5 Charge, discharge curves and cycling performance for doped LiFePO_4 . (a1) Discharge capacity of LFP/PEG/ZnO (2 wt.%) at different C-rates (0.1–10C) (a1), cycle performance comparison of LFP, LFP/PEG and LFP/PEG/ZnO discharge capacity at C/10 (a2); initial discharge curves (b1) and cycling performance (b2) of LiFePO_4 and Ti^{4+} -doped LiFePO_4 synthesized at 600°C ; discharge curves (c1) and cycle stability (c2) of doped LFP/CA at room temperature).^{74, 75, 76}

capacity of $\text{Li}_3\text{V}_{1.95}\text{Sn}_{0.05}(\text{PO}_4)_3/\text{C}$ was 136 mAh g^{-1} (Fig. 4b1,b2).⁷³ Cu-added and Ag-added LiFePO_4 electrode did not contribute to the growth of small particles and reduce the resistance between the particles and improves its kinetics in terms of capacity delivery and cycle life.³² LFP particles were synthesized by solid state reaction method and ball milled with PEG based ZnO nano-powders to form ZnO/C co-coated LFP

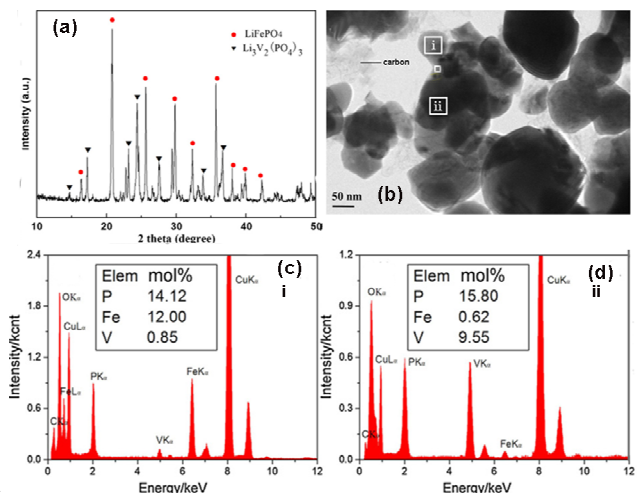


Fig. 6 XRD pattern of $\text{LiFePO}_4\text{-Li}_3\text{V}_2(\text{PO}_4)_3$ synthesized at 700°C for 12 h (a); TEM images of $9\text{LiFePO}_4\cdot\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (b); EDS spectra of regions i (c), ii (d) (Region i and ii are in b).^{79, 80}

particles. LFP/PEG/ZnO (2 wt.%) composite electrode showed a maximum discharge capacity of 158.9 mAh g^{-1} at 0.1C and 145.7 mAh g^{-1} at 5C and 109.3 mAh g^{-1} at 10C, respectively. Without fading for LFP/PEG/ZnO (2 wt.%) composite electrode after 50 cycles at 0.1C rate (Fig. 5a1,a2).⁷⁴ Ti^{4+} -doped LiFePO_4 was prepared by an ambient-reduction and post-sintering method. Electrochemical properties of lithium iron phosphate with Ti^{4+} -doping has been significantly improved. The Ti^{4+} -doped sample sintered at 600°C delivers an initial discharge capacity of 150, 130 and 125 mAh g^{-1} at 0.1C, 1C and 2C rates, respectively, there was negligible drop in capacity after 40 cycle (Fig. 5b1,b2).⁷⁵ Mg-doped LiFePO_4 and pure LiFePO_4 were prepared by low-temperature sol-gel method using succinic acid as a chelating agent. $\text{LiMg}_{0.05}\text{Fe}_{0.95}\text{PO}_4$ shows initial charge and discharge capacities of 159 and 141 mAh g^{-1} at 0.2 C rate respectively, as compared to 121 and 107 mAh g^{-1} of pure LiFePO_4 . After 60 circles the $\text{LiMg}_{0.05}\text{Fe}_{0.95}\text{PO}_4$ capacity retention rate is still more than 89%.⁶⁷ The olivine-type lanthanum and magnesium doped $\text{Li}_{0.99}\text{La}_{0.01}\text{Fe}_{0.9}\text{Mg}_{0.1}\text{PO}_4/\text{carbon aerogel}$ composite is synthesized via a simple solution impregnation process using carbon aerogel (CA) as templates. The capacity reaches to 160.2 mAh g^{-1} , 154.3 mAh g^{-1} , 142.7 mAh g^{-1} , 135.7 mAh g^{-1} , 124.3 mAh g^{-1} and 101.8 mAh g^{-1} under the discharge rates 0.2 C, 1C, 5C, 10C, 20C, 50 C, respectively at room temperature (20°C) (Fig. 5c1,c2).⁷⁶ Dy doping and carbon coating are used to synthesize a LiFePO_4 composite cathode material in a simple solution. $\text{LiDy}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ composite cathode shows its initial discharge capacity of 153 mAh g^{-1} at 0.1 C. The electronic conductivity of Dy doped LiFePO_4/C was enhanced to $1.9 \times 10^{-2} \text{ S cm}^{-1}$.⁷⁷

Single dopants play a big role in improving the electrochemical properties of both LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Single doping element is uniformly distributed over all the particles, homogeneous doping can effectively inhibit the growth of crystalline grain, reduce the crystal particle diameter. The radius of dopants which are smaller than Fe, V, or Li, the composition powder has smaller lattice constants and unit cell volume than LFP or LVP. On the contrary, the radius of dopants are larger, the lattice constants and unit cell volume of the composition powder are larger. In addition, single dopants would not alter the structure of materials, and resulted in electron holes in the structure which will be beneficial to the electrochemical performance of cathode materials.

Dual(Mutual) doping and composite material modification

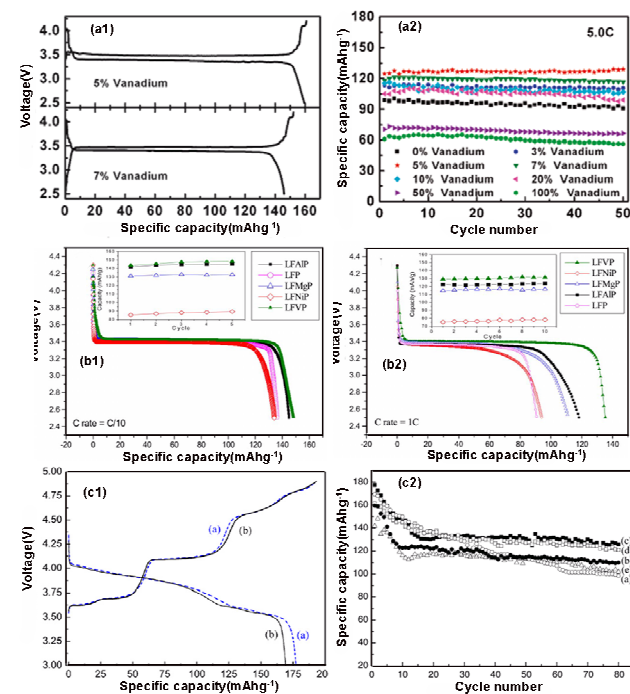


Fig. 7 Charge/discharge and cyclic performances of samples for Fe^{2+} , V^{3+} mutual doping. (Charge/discharge profiles of samples at 0.1 C (a1) and cyclic performances of samples at 5.0 C rates (a2); the discharge curves of $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4$ samples under C/10 at the 10th cycle (b1), and the discharge curves of $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4$ samples under 1C rate at the 10th cycle (b2); typical charge/discharge curves of Fe-doped (a) and undoped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (b) (c1), and discharge capacity as a function of cycle number at C/5 rate and 25 °C for various $\text{Li}_3\text{Fe}_x\text{V}_{2-x}(\text{PO}_4)_3$. (a) $x = 0.00$; (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.04$ and (e) $x = 0.06$ (c2)).^{21, 45, 71}

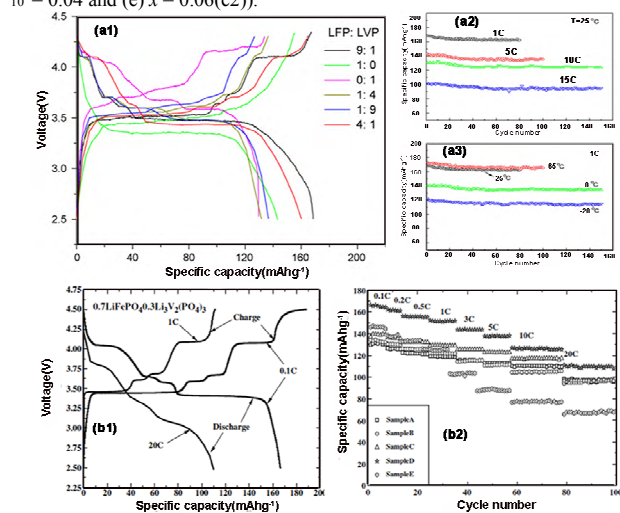


Fig. 8 Charge/discharge and cyclic performances of samples for $x\text{LiFePO}_4 \cdot y\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites. (The first charge/discharge curves of the $x\text{LiFePO}_4 \cdot y\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composites (a1) and cycling performance of $9\text{LiFePO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (a2) at different discharge rates and (a3) at different working temperatures; charge-discharge curves of samples D (b1) and cycle performance of the samples at different discharge rates (b2)).^{46, 81}

Because of the structures of LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and preparation methods are similar, Fe^{2+} and V^{3+} mutual doping may be unavoidable during the calcining process of preparing LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composites materials. That is, Fe^{2+} (or/and Li^+) in LiFePO_4 may be substituted by V,^{55,78} and V^{3+} (or/and Li^+) in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ may be substituted by Fe.²¹ XRD pattern (Fig. 6a), EDS spectra of regions i (Fig. 6c), ii (Fig. 6d) which taken from the TEM images of $9\text{LiFePO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$

(Fig. 6b) correspond to the V-doped LiFePO_4 and Fe-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, indicating the synthesized compound is a mixture of LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.^{79,80}

$\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$ samples were synthesized using a two-step solid-state reaction route. Experiments show that V incorporation significantly enhances the electrochemical performance of LiFePO_4 . Particularly, the LiFePO_4/C sample with 5 wt.% vanadium doping shows the best performance with a specific discharge capacity of 129 mAh g^{-1} at 5C after 50 cycles; the capacity retention ratio is over than 97.5% at 0.1C 1C 2C and 5C (Fig. 7a1,a2).⁴⁵ Mg^{2+} , Ni^{2+} , Al^{3+} , or V^{3+} ion was doped into the Fe site to synthesize $\text{LiFe}_{0.95}\text{M}_{0.05}\text{PO}_4$ samples using a solution method, which atomic radius similar to or smaller than that of Fe^{2+} ion. All samples contain a carbon content of about 3 wt.% and have a similar Brunauer–Emmett–Teller surface area. The $\text{LiFe}_{0.95}\text{V}_{0.05}\text{PO}_4$ powder with the largest volume of unit cells (longest Li–O bond length) exhibits the highest discharging capacity of 152 and 136 mAh g^{-1} at 0.1C and 1C rates, respectively (Fig. 7b1,b2).⁷¹ The Fe-doped $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathode materials for Li-ion batteries were synthesized by a conventional solid-state reaction. The initial discharge capacity of $\text{Li}_3\text{Fe}_{0.02}\text{V}_{1.98}(\text{PO}_4)_3$ was 177 mAh g^{-1} and 126 mAh g^{-1} after the 80th cycle. The retention rate of discharge capacity is about 71%, much higher than 58% of the undoped system (Fig. 7c1,c2).²¹ $9\text{LiFePO}_4 \cdot \text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was synthesized via a carbon thermal reaction using petroleum coke as reduction agent and carbon source. Fig. 8a1,a2,a3 shows the electrochemical properties. The first discharge capacity of $9\text{LFP-LVP}/\text{C}$ in 18650 type cells is 168 mAh g^{-1} at 1C, and shows high reversible discharge capacity of 125 mAh g^{-1} at 10 C even after 150 cycles. At the temperature of -20°C , the reversible capacity of $9\text{LFP-LVP}/\text{C}$ can maintain 75% of that at room temperature.⁴⁶ Hybrid materials $x\text{LiFePO}_4 \cdot (1-x)\text{Li}_3\text{V}_2(\text{PO}_4)_3$ were synthesized through sol–gel method. The sample $0.7\text{LiFePO}_4 \cdot 0.3\text{Li}_3\text{V}_2(\text{PO}_4)_3$ inherits the advantages of LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, exhibiting an initial discharge capacity of 166 mAh g^{-1} at 0.1 C rate and 109 mAh g^{-1} at 20 C rate, with a capacity retention rate of 73.3% and an excellent cycle stability. $x\text{LiFePO}_4 \cdot (1-x)\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ($x = 0, 0.3, 0.5, 0.7, 1$ corresponding to the A, B, C, D, E). The electrochemical performances of $x\text{LiFePO}_4 \cdot (1-x)\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are shown in Fig. 8b1 and b2.⁸¹

Compared with the single dopants, large number of defects can be also produced by the dual dopants (especially for Fe, V) this would greatly improve the electrochemical properties of the materials. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has inherently high ionic conductivity, the large polyanion helping to stabilize the structure in an open 3D framework and allowing a fast ion migration. Binding LiFePO_4 and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ together would obtain more Li^+ transport channel, so V-doped LFP and Fe-doped LVP played great part on electrons transfer activity and the lithium ion diffusivity in the composite materials.

The direction of the future

With the various aspects performance of the lithium vanadium phosphate and lithium iron phosphate gradually explored by human, however, there are a plenty of problems still unresolved. These problems classified as follows.

The relationship between the power performance and the electrode/electrolyte interface is still mysterious. Stability of nano-sized LiFePO_4 in the atmosphere is bad. Poor low-temperature performance and the low tap density were seriously limits the volumetric power density of a lithium-ion battery that to be used in portable device.

Further work is needed to ensure that the lithium iron

phosphate and lithium vanadium phosphate batteries can withstand operation on EVs or HEVs and other equipment.

Conclusion

LiFePO₄ and Li₃V₂(PO₄)₃ with varieties of modification strategies have improved the electrochemical properties. Doping modification and composite modification as the main exploration content appears in this article, and some remain obstacles about LiFePO₄ and Li₃V₂(PO₄)₃.

Single and dual dopants (act as composite modification in a different way) are compared in this article. The influence of the single dopants technology for anode materials such as lithium iron phosphate and lithium vanadium phosphate has been matured. Composite materials would be formed by dual dopants, and the composite materials inherited their advantages especially. According to our comparison, single dopants paved the way for dual dopants modification.

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